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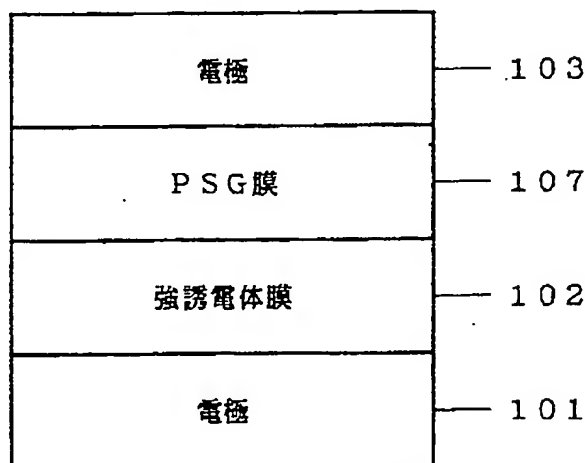
(54) 【発明の名称】 記憶装置

(57) 【要約】

【目的】 ペロブスカイト結晶構造を持つチタン酸ジルコニウム鉛 (P Z T) 系等の強誘電体膜から成る記憶装置の劣化を防止し、記憶回数と寿命の向上を図る。

【構成】 強誘電体膜表面に燐ガラス膜を形成する。第1の電極である P t / T i 膜からなる電極膜 1 0 1 上には強誘電体膜 1 0 2 が形成され、該強誘電体膜 1 0 2 上には燐ガラス膜 1 0 7 が形成され、該燐ガラス膜 1 0 7 上には第2の電極である T i / P t 膜から成る電極膜 1 0 3 が形成されて成る。また強誘電体膜側面に燐ガラス膜を形成する、あるいは強誘電体膜表面を粗構造とすること等。

【効果】 結晶格子内の酸素欠損を補償する酸化剤を付加するかあるいは自己補償を可能にするために強誘電体膜の少なくとも表面を粗状にすることにより、強誘電体膜の劣化を防止することができる。書換え回数が10億回以上で、10年以上の寿命のある記憶装置を提供できる。



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## 【特許請求の範囲】

【請求項1】 強誘電体膜表面には燐ガラス膜が形成されて成ることを特徴とする記憶装置。

【請求項2】 少なくとも強誘電体膜側面には燐ガラス膜が形成されて成ることを特徴とする記憶装置。

【請求項3】 少なくとも強誘電体膜表面は粗構造であることを特徴とする記憶装置。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は強誘電体膜から成る記憶装置の記憶膜構成と記憶膜構造に関する。

【0002】

【従来の技術】 従来、強誘電体膜から成る記憶装置は、R. Womack, D. Tolsh, ISSCC Technical Digest, 242(1989)などに示されているごとく、チタン酸ジルコニウム鉛(PZT)などの強誘電体膜を白金膜電極などで挟まれて形成されて成るのが通例であった。

【0003】

【発明が解決しようとする課題】 しかし、上記従来技術によるとチタン酸ジルコニウム鉛(PZT)などの強誘電体膜などの記憶回数がせいぜい100万回程度の書換えて劣化したり、記憶寿命がせいぜい2年間程度であるという課題があった。

【0004】 本発明は、かかる従来技術の課題を解決し強誘電体膜から成る記憶装置の記憶回数と記憶寿命の向上を図ることを目的とする。

【0005】

【課題を解決するための手段】 上記課題を解決し、上記目的を達成するために、本発明は、記憶装置に関し、

(1) 強誘電体膜表面に燐ガラス膜を形成すること、および(2) 少なくとも強誘電体膜側面に燐ガラス膜を形成すること、および(3) 少なくとも強誘電体膜表面を粗構造とすること、などの手段を取る。

【0006】

【作用】 ペロブスカイト結晶構造を持つチタン酸ジルコニウム鉛(PZT)系などの強誘電体膜の劣化の原因は、結晶格子内に酸素欠損を起こすためであり、この酸素欠損を補償する酸化剤を付加するかあるいは自己補償を可能にするために強誘電体膜の少なくとも表面を粗状にすることにより、強誘電体膜の劣化を防止することができる作用が出る。

【0007】

【実施例】 以下、実施例により本発明を詳述する。

【0008】 図1は、本発明の一実施例を示す記憶部の原理的な断面図である。すなわち、第1の電極であるPt/Ti膜からなる電極膜101上には強誘電体膜102が形成され、該強誘電体膜102上には燐ガラス膜107が形成され、該燐ガラス膜107上には第2の電極であるTi/Pt膜から成る電極膜103が形成されて成る。

【0009】 この記憶装置の製法は、SiまたはGaAsなどの半導体基板上にSiO<sub>2</sub>やSi<sub>3</sub>N<sub>4</sub>などの絶縁膜を形成し、該絶縁膜にコンタクト穴開けをして、半導体基板のコンタクト穴部を介してスパッタ蒸着やCVD法などによりTi膜を100nm厚さ程度形成し、下地がSiの場合は該Ti膜表面をNH<sub>3</sub>雰囲気中で800度、30秒程度的高速熱処理(RTP)により電気伝導性のあるTiN膜としてSiの拡散に対する障壁膜として、Pt膜を50nm厚さ程度スパッタ蒸着して第1の電極膜101とし、該第1の電極膜101上にアルコール基のPZTなどの原液を塗布するいわゆるゾルゲル法あるいはスピノングラス(SOG)法あるいは金属有機デポジション(MOCVD)法と呼ばれる方法や有機金属蒸気を用いた化学蒸着(CVD)法により130nm厚さ程度に電氣的書き込み消去記憶装置の場合はPZTなどから成る強誘電体膜102を形成し、酸素雰囲気中でアニールした後、CVD法により燐濃度が4~10モル%程度の燐ガラス(PSG)膜107を1nm~100nm厚さ程度形成後、第2の電極膜103をスパッタ蒸着法などによりPt膜とTi膜を形成したりその他のAlなどの金属膜などを形成する。

【0010】 この記憶装置における燐ガラス膜107の作用は酸化剤としての作用であり、強誘電体膜102に電界が印加された場合にこれら強誘電体膜107の結晶内で欠乏する酸素を補給するためのものである。よってこの燐ガラス膜107はP<sub>2</sub>O<sub>5</sub>単体であっても良く、P<sub>2</sub>O<sub>5</sub>以外の5酸化マンガンや過マンガン酸カリや硝酸カリの単体膜や5酸化マンガンや過マンガン酸カリや硝酸カリなどの酸化剤を含んだ膜であれば良く強誘電体膜102にこれら酸化剤や酸化剤を含んだガラスなどを含有させたり混合させたりしても良い。また、この酸化剤を含んだ膜は必ずしも強誘電体膜102の上部表面のみならず下部表面あるいは中間層として形成されても良い。なお、P<sub>2</sub>O<sub>5</sub>などの酸化剤は吸湿性であるので、単体膜や高濃度膜を形成する場合にはさらに低濃度膜やSiO<sub>2</sub>膜やSi<sub>3</sub>N<sub>4</sub>膜などの絶縁膜を形成して耐湿性を向上しておく必要がある。

【0011】 強誘電体膜に酸化剤からの酸素を補給することができるようにすることにより、記憶装置の書換え回数き換え回数を10億回以上にし寿命を10年以上にすることができる。

【0012】 図2は、本発明の他の実施例を示す、半導体記憶装置の記憶要部の断面図である。すなわち、Si104には不純物の拡散層105およびSiO<sub>2</sub>膜106が形成されて成り、該SiO<sub>2</sub>膜106にはコンタクト穴が開けられ、該コンタクト穴を介して第1の電極であるPt/Ti膜やPt/TiN/TiN膜などから成る電極膜101が前記拡散層105と接続されて形成され、前記第1の電極である電極膜101上には強誘電体膜102が形成されて成り、該強誘電体膜102上に

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は第2の電極であるTi/Pt膜から成る電極膜103が形成されて成り、半導体記憶装置の記憶部を形成して成り、該記憶部の少なくとも強誘電体膜102の側面を含む表面には燐濃度4~10モル%、厚さ10~100nm程度の燐ガラス膜107が形成されて成る。

【0013】この記憶装置における燐ガラス膜107の作用は酸化剤としての作用であり、強誘電体膜102に電界が印加された場合にこれら強誘電体膜102の結晶内で欠乏する酸素を強誘電体膜102の側面から補給するためのものである。また、この燐ガラス膜107はP<sub>2</sub>O<sub>5</sub>単体であっても良く、P<sub>2</sub>O<sub>5</sub>以外の5酸化マンガ

【0014】さらにこの燐ガラス膜107は強誘電体膜102を、たとえばストライプ状やチェック状にエッチングしたり10~100nm程度粗な凹凸を形成したりして、その少なくとも側面を含む表面などに形成し、さらにその上下に電極膜が形成されていても良い。

【0015】強誘電体膜の少なくとも側面に酸化剤や酸化剤を含んだガラス膜などを形成することにより、記憶装置の書換え回数き換え回数を10億回以上にし寿命を10年以上にすることができる。

【0016】図3は本発明のその他の実施例を示す、半導体記憶装置の記憶要部の断面図である。すなわち、Si104には不純物の拡散層105およびSiO<sub>2</sub>膜106が形成されて成り、該SiO<sub>2</sub>膜106にはコンタクト穴が開けられ、該コンタクト穴を介して第1の電極であるPt/Ti膜から成る電極膜101が前記拡散層105と接続されて形成されて成ると共に該第1の電極である電極膜101の表面は粗に形成されて成り、該第1の電極である10~100nm程度に粗な電極膜101上には強誘電体膜102が少なくともその表面が10~100nm程度に粗に形成されて成り、該粗表面の強誘電体膜102上には第2の電極であるTi/Pt膜から成る電極膜103が形成されて成り、半導体記憶装置の記憶部を形成して成る。

【0017】強誘電体膜を粗構造にするのは表面のみならず強誘電体膜内や強誘電体膜下表面であっても良く、たとえば電極101の表面をホットエッチングなどや下地にポリSiを球状結晶粒にCVD法で550度で育成してその上に電極101を形成するなどして電極101の表面を10~100nm程度の凹凸状の粗構造にしてから強誘電体膜102を形成したり、強誘電体膜102の

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表面をホットエッチングやCVD法により強誘電体を球状結晶粒化するなどして、強誘電体膜102の表面を凹凸状の10~100nm程度の粗構造にしてから電極103を形成するなどしても良い。

【0018】強誘電体膜を10~100nm程度の粗構造にすると、電界を強誘電体膜に印加した場合に、強誘電体膜の厚さの差により、分極を起こす部分と起こさない部分とが生じ、分極を起こした部分から逸脱する酸素原子を分極を起こしていない部分にある酸素原子で補償するいわゆる自己補償機能を持たせることができる作用があり、記憶装置の書換え回数き換え回数を10億回以上にし寿命を10年以上にすることができる。

【0019】なお、強誘電体膜を10~100nm程度の粗構造にしてかつ強誘電体膜の表面や側面に酸化剤膜を形成したり、強誘電体膜に酸化剤や酸化剤を含んだガラスなどを含有させたり混合させたりしても良いことは言うまでもない。

【0020】なお、強誘電体膜としては、チタン酸ジルコニウム鉛の他、チタン酸バリウムやチタン酸ストロンチウムやチタン酸ビスマスなどがある。

【0021】この強誘電体膜の表面や側面に酸化剤を含んだガラス膜や酸化剤膜を形成したり含有あるいは混合させたり、強誘電体膜を10~100nm程度の粗構造にしたりする方法は、E.Fujili, et.al., IEDM Technical Digest, 267(1992)に示されている誘電率400程度のチタン酸バリウムストロンチウムから成る高誘電体膜や、P.C.Pazan et.al., IEDM Technical Digest, 263(1992)に示されている誘電率21程度の酸化タンタル膜などのごとく、ダイナミックランダムアクセスメモリのキャパシタ記憶部に用いられる高誘電体膜にも適用することができ、この場合には高誘電体膜のリーク電流を減少することができ、記憶保持時間の増大とそれに伴うレック時間の延長と低消費電力化などを図ることができる。

【0022】

【発明の効果】本発明により書換え回数が10億回以上で、10年以上の寿命のある記憶装置を提供することができる効果がある。

【図面の簡単な説明】

【図1】本発明の一実施例を示す記憶部の原理的な断面図である。

【図2】本発明の他の実施例を示す、半導体記憶装置の記憶要部の断面図である。

【図3】本発明のその他の実施例を示す、半導体記憶装置の記憶要部の断面図である。

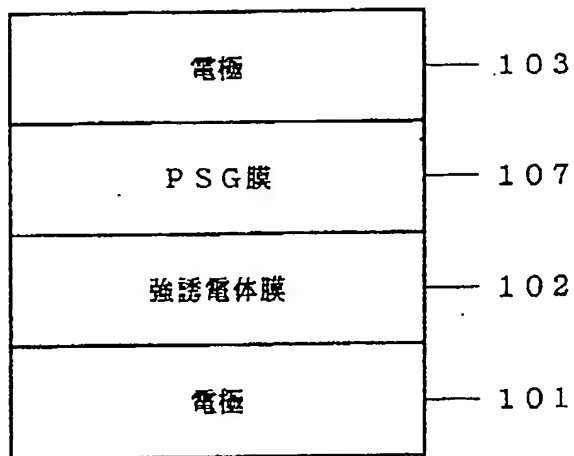
【符号の説明】

101・・・電極膜  
102・・・強誘電体膜  
103・・・電極膜  
104・・・Si  
105・・・拡散層

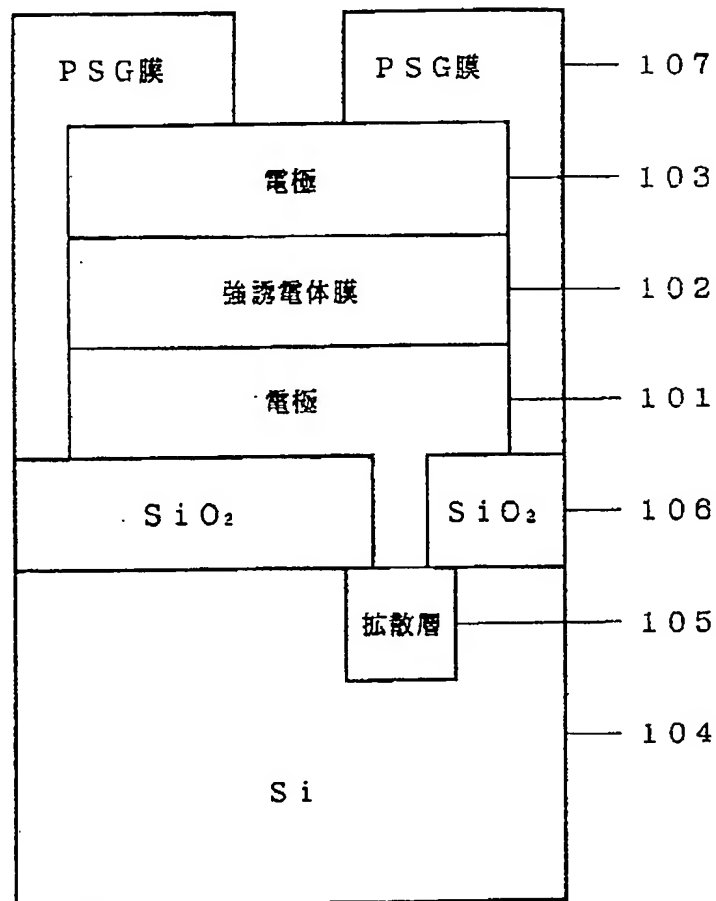
106... $\text{SiO}_2$ 膜

107...燐ガラス膜

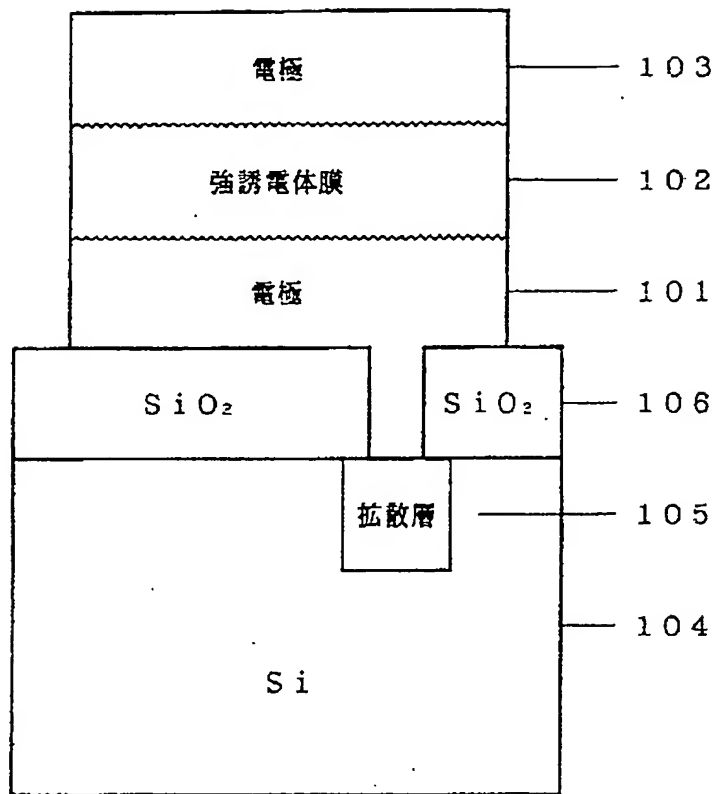
【図1】



【図2】



【図3】



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**CLAIMS**

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[Claim(s)]

[Claim 1] Storage characterized by forming phosphorus glass membrane in a ferroelectric film front face, and changing.

[Claim 2] Storage characterized by forming phosphorus glass membrane in a ferroelectric film side face at least, and changing.

[Claim 3] A ferroelectric film front face at least is storage characterized by being rough structure.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the storage film configuration and storage membrane structure of storage which consist of the ferroelectric film.

[0002]

[Description of the Prior Art] Ferroelectric film, such as titanate-acid zirconium lead (PZT), is inserted with a platinum membrane electrode etc., it is formed, and usually changed as the storage which consists of the ferroelectric film was conventionally shown in R.Womack, D.Tolsh, ISSCC Technical Digest, 242 (1989), etc.

[0003]

[Problem(s) to be Solved by the Invention] However, according to the above-mentioned conventional technique, it deteriorated by rewriting whose counts of storage, such as ferroelectric film, such as titanate-acid zirconium lead (PZT), are about at most 1 million times, and the technical problem that a storage life was an at most two-year about room occurred.

[0004] This invention aims at aiming at the count of storage of storage and the improvement in a storage life which solve the technical problem of this conventional technique and consist of the ferroelectric film.

[0005]

[Means for Solving the Problem] that this invention forms phosphorus glass membrane in (1) ferroelectric film front face about storage in order to solve the above-mentioned technical problem and to attain the above-mentioned purpose, and (2) -- forming phosphorus glass membrane in a ferroelectric film side face at least, and (3) -- means, such as making a ferroelectric film front face into rough structure at least, are taken.

[0006]

[Function] The cause of degradation of ferroelectric film, such as a titanate-acid zirconium lead (PZT) system with a perovskite crystal structure, is for starting an oxygen deficiency in a crystal lattice, and in order to add the oxidizer with which this oxygen deficiency is compensated or to enable self-compensation, the operation which can prevent degradation of the ferroelectric film comes out of it by [ of the ferroelectric film ] making a front face into rough \*\* at least.

[0007]

[Example] Hereafter, this invention is explained in full detail according to an example.

[0008] Drawing 1 is the theoretic sectional view of the storage section showing one example of this invention. That is, the ferroelectric film 102 is formed on the electrode layer 101 which consists of Pt/Ti film which is the 1st electrode, the phosphorus glass membrane 107 is formed on this ferroelectric film 102, the electrode layer 103 which consists of the Ti/Pt film which is the 2nd electrode is formed on this phosphorus glass membrane 107, and it changes.

[0009] The process of this storage forms insulator layers, such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, on semi-conductor substrates, such as Si or GaAs, and carries out contact perforation to this insulator layer. 100nm thickness extent formation of the Ti film is carried out with sputter vacuum evaporation, a CVD method, etc. through the contact hole of a semi-conductor substrate. When a substrate is Si, this Ti film front face is used as the obstruction film to diffusion of Si as TiN film which has electrical conductivity in NH<sub>3</sub> ambient atmosphere by high-speed heat treatment (RTP) for 800 degrees and about 30 seconds. Carry out 50nm thickness extent sputter vacuum evaporation of the Pt film, and it considers as the 1st electrode layer 101. the so-called sol gel process which applies undiluted solutions, such as PZT of an alcoholic radical, on this 1st electrode layer 101, or a spin-on glass (SOG) -- low or metal organic deposition (MOCVD) -- the chemical vacuum deposition (CVD) using the approach and organic metal steam which are called low -- by low In the case of electric write-in elimination storage, the ferroelectric film 102 which consists of PZT etc. is formed in 130nm thickness extent. After annealing in an oxygen ambient atmosphere, the phosphorus glass (PSG) film 107 whose phosphorus concentration is about 4-10 mol % with a CVD method After 1nm - 100nm thickness extent formation, Pt film and Ti film are formed for the 2nd electrode layer 103 with sputter vacuum deposition etc., or metal membranes, such as other aluminum, etc. are formed.

[0010] An operation of the phosphorus glass membrane 107 in this storage is an operation as an oxidizer, and when electric field are impressed to the ferroelectric film 102, it is for supplying the oxygen which runs short within the crystal of these ferroelectric film 107. Therefore, 107 may make the glass which contained these oxidizers and an oxidizer in the ferroelectric film 102 that to be P<sub>2</sub>O<sub>5</sub> this phosphorus glass membrane 5 simple substance, and what is necessary is just the film containing oxidizers, such as the simple substance film, 5 manganese oxide and potassium permanganate of 5 manganese oxide and potassium permanganates other than P<sub>2</sub>O<sub>5</sub>, or nitric-acid potash, and nitric-acid potash, contain, or may be mixed. Moreover, the film containing this oxidizer may not necessarily be formed as not only the up front face of the ferroelectric film 102 but a lower front face, or an interlayer. In addition, since oxidizers, such as P<sub>2</sub>O<sub>5</sub>, are hygroscopicity, when forming the simple substance film and the high concentration film, they need to form insulator layers, such as low concentration film, SiO<sub>2</sub> film, and Si<sub>3</sub>N<sub>4</sub> film, further, and need to improve moisture resistance.

[0011] By enabling it to supply the oxygen from an oxidizer to the ferroelectric film, it can come the number of rewritings of storage, the count of a substitute can be made into 1 billion times or more, and a life can be carried out in 10 or more.



[0012] Drawing 2 is the sectional view of the storage important section of a semiconductor memory showing other examples of this invention. Namely, the diffusion layer 105 of an impurity and SiO<sub>2</sub> film 106 are formed in Si104, and it changes. A contact hole can open in this SiO<sub>2</sub> film 106, and connect with said diffusion layer 105 and the electrode layer 101 which consists of the Pt/Ti film which is the 1st electrode, the Pt/TiN/TiN film, etc. through this contact hole is formed. Strong \*\*\*\*\* 102 is formed on the electrode layer 101 which is said 1st electrode, and it changes. On this ferroelectric film 102, the electrode layer 103 which consists of the Ti/Pt film which is the 2nd electrode is formed, and it changes. The storage section of a semiconductor memory is formed and it changes, and the with a phosphorus concentration thickness [ about 10-100nm in % and thickness of 4-10 mols ] phosphorus glass membrane 107 is formed in the front face of this storage section which includes the side face of the ferroelectric film 102 at least, and it grows into it.

[0013] An operation of the phosphorus glass membrane 107 in this storage is an operation as an oxidizer, and when electric field are impressed to the ferroelectric film 102, it is for supplying the oxygen which runs short within the crystal of these ferroelectric film 102 from the side face of the ferroelectric film 102. Moreover, 107 may be P<sub>2</sub>O<sub>5</sub> this phosphorus glass membrane 5 simple substance, and should just be the film containing oxidizers, such as the simple substance film, manganese oxide and potassium permanganate of 5 manganese oxide and potassium permanganates other than P<sub>2</sub>O<sub>5</sub>, or nitric-acid potash, and nitric-acid potash. Moreover, the film containing this oxidizer may not necessarily be formed as not only the up front face of the ferroelectric film 102 but a lower front face, or an interlayer. In addition, since oxidizers, such as P<sub>2</sub>O<sub>5</sub>, are hygroscopicity, when forming the simple substance film and the high concentration film, they need to form insulator layers, such as low concentration film, SiO<sub>2</sub> film, and Si<sub>3</sub>N<sub>4</sub> film, further, and need to improve moisture resistance.

[0014] Furthermore, this phosphorus glass membrane 107 etches the ferroelectric film 102 the shape for example, of a stripe, and in the shape of a check, or forms irregularity \*\*\*\* about 10-100nm, and forms it in that front face that includes a side face at least, and the electrode layer may be further formed in those upper and lower sides.

[0015] By forming the glass membrane containing an oxidizer or an oxidizer of the ferroelectric film etc. in a side face at least, it can come the number of rewritings of storage, the count of a substitute can be made into 1 billion times or more, and a life can be carried out in 10 or more.

[0016] Drawing 3 is the sectional view of the storage important section of a semiconductor memory showing the example of others of this invention. Namely, the diffusion layer 105 of an impurity and SiO<sub>2</sub> film 106 are formed in Si104, and it changes. A contact hole can open in this SiO<sub>2</sub> film 106, and the front face of the electrode layer 101 which is this 1st electrode while connecting with said diffusion layer 105, forming the electrode layer 101 which consists of the Pt/Ti film which is the 1st electrode through this contact hole and changing is formed in \*\*, and changes. On the \*\*\*\* electrode layer 101 which is this 1st electrode, the ferroelectric film 102 is formed at least in about 10-100nm by about 10-100nm at

\*\*, and the front face turns to it. On the ferroelectric film 102 on this front face of rough, the electrode layer 103 which consists of the Ti/Pt film which is the 2nd electrode is formed, and it changes, and the storage section of a semiconductor memory is formed and it changes.

[0017] Not only a front face but the inside of the ferroelectric film and the bottom front face of the ferroelectric film may make the ferroelectric film rough structure. for example, raise Pori Si for the front face of an electrode 101 at 550 degrees with a CVD method on photoetching etc. and a substrate at a spherical crystal grain, form an electrode 101 on it, after making the front face of an electrode 101 into about 10-100nm concave convex rough structure, form the ferroelectric film 102, or After carrying out spherical crystal granulation of the ferroelectric for the front face of the ferroelectric film 102 with photoetching or a CVD method and making the front face of the ferroelectric film 102 into about 10-100nm concave convex rough structure, you may carry out forming an electrode 103 etc.

[0018] When the ferroelectric film was made into about 10-100nm rough structure and electric field are impressed to the ferroelectric film, according to the difference of the thickness of the ferroelectric film The part which causes polarization, and the part which is not raised arise and there is an operation which can give the so-called self-compensation function to compensate the oxygen atom which deviates from the part which caused polarization with the oxygen atom in the part which has not caused polarization. It can come the number of rewritings of storage, the count of a substitute can be made into 1 billion times or more, and a life can be carried out in 10 or more.

[0019] In addition, it cannot be overemphasized that the ferroelectric film is made into about 10-100nm rough structure, and the glass which contained the oxidizer and the oxidizer in the ferroelectric film may be made to contain, or you may make it, and mix. [ forming the oxidizer film in the front face and side face of the ferroelectric film ]

[0020] In addition, as ferroelectric film, there are others and titanate-acid BARYUM and titanate-acid stolon CHUMU, a titanate-acid bismuth, etc. [ lead / titanate-acid zirconium ]

[0021] The approach which, and is contained mixed, or has mixed the ferroelectric film enough about 10-100nm rough structure, and is carried out [ an approach ] [ forming the glass membrane and the oxidizer film containing an oxidizer in the front face and side face of this ferroelectric film ] E. The high dielectric film which consists of Fujili, et.al., IEDM Technical Digest, and with a dielectric constant of about 400 shown in 267 (1992) titanate-acid BARYUM stolon CHUMU, P. like C.Fazan et.al., IEDM Technical Digest, the with a dielectric constant of about 21 shown in 263 (1992) tantalum oxide film, etc. Are applicable also to the high dielectric film used for the capacitor storage section of dynamic random access memory. In this case, the leakage current of a high dielectric film can be decreased and increase of memory holding time, extension of the REFRESH time amount accompanying it, low-power-ization, etc. can be attained.

[0022]

[Effect of the Invention] It is effective in the ability to offer the storage with which

it rewrites by this invention and ten years or more of life has a count by 1 billion times or more.

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TECHNICAL FIELD

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[Industrial Application] This invention relates to the storage film configuration and storage membrane structure of storage which consist of the ferroelectric film.

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PRIOR ART

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[Description of the Prior Art] Ferroelectric film, such as titanate-acid zirconium lead (PZT), is inserted with a platinum membrane electrode etc., it is formed, and usually changed as the storage which consists of the ferroelectric film was conventionally shown in R.Womack, D.Tolsh, ISSCC Technical Digest, 242 (1989), etc.

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EFFECT OF THE INVENTION

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[Effect of the Invention] It is effective in the ability to offer the storage with which it rewrites by this invention and ten years or more of life has a count by 1 billion times or more.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, according to the above-mentioned conventional technique, it deteriorated by rewriting whose counts of storage, such as ferroelectric film, such as titanate-acid zirconium lead (PZT), are about at most 1 million times, and the technical problem that a storage life was an at most two-year about room occurred.

[0004] This invention aims at aiming at the count of storage of storage and the improvement in a storage life which solve the technical problem of this conventional technique and consist of the ferroelectric film.

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MEANS

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[Means for Solving the Problem] that this invention forms phosphorus glass membrane in (1) ferroelectric film front face about storage in order to solve the above-mentioned technical problem and to attain the above-mentioned purpose, and (2) -- forming phosphorus glass membrane in a ferroelectric film side face at least, and (3) -- means, such as making a ferroelectric film front face into rough structure at least, are taken.

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## OPERATION

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[Function] The cause of degradation of ferroelectric film, such as a titanic-acid zirconium lead (PZT) system with a perovskite crystal structure, is for starting an oxygen deficiency in a crystal lattice, and in order to add the oxidizer with which this oxygen deficiency is compensated or to enable self-compensation, the operation which can prevent degradation of the ferroelectric film comes out of it by [ of the ferroelectric film ] making a front face into rough \*\* at least.

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## EXAMPLE

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[Example] Hereafter, this invention is explained in full detail according to an example.

[0008] Drawing 1 is the theoretic sectional view of the storage section showing one example of this invention. That is, the ferroelectric film 102 is formed on the electrode layer 101 which consists of Pt/Ti film which is the 1st electrode, the phosphorus glass membrane 107 is formed on this ferroelectric film 102, the electrode layer 103 which consists of the Ti/Pt film which is the 2nd electrode is formed on this phosphorus glass membrane 107, and it changes.

[0009] The process of this storage forms insulator layers, such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, on semi-conductor substrates, such as Si or GaAs, and carries out contact perforation to this insulator layer. 100nm thickness extent formation of the Ti film is carried out with spatter vacuum evaporatio~~no~~, a CVD method, etc. through the contact hole of a semi-conductor substrate. When a substrate is Si, this Ti film front face is used as the obstruction film to diffusion of Si as TiN film which has electrical conductivity in NH<sub>3</sub> ambient atmosphere by high-speed heat treatment (RTP) for 800 degrees and about 30 seconds. Carry out 50nm thickness extent spatter vacuum evaporatio~~no~~ of the Pt film, and it considers as the 1st electrode layer 101. the so-called sol gel process which applies undiluted solutions, such as PZT of an alcoholic radical, on this 1st electrode layer 101, or a spin-on glass (SOG) -- law or metal organic deposition (MOCVD) -- the chemical vacuum deposition (CVD) using the approach and organic metal steam which are called law -- by law In the case of electric write-in elimination storage, the ferroelectric film 102 which consists of PZT etc. is formed in 130nm thickness extent. After annealing in an oxygen ambient atmosphere, the phosphorus glass (PSG) film 107 whose phosphorus concentration is about 4-10 mol % with a CVD method After 1nm - 100nm thickness extent formation, Pt film and Ti film are formed for the 2nd electrode layer 103 with spatter vacuum deposition etc., or metal membranes, such as other aluminum, etc. are formed.

[0010] An operation of the phosphorus glass membrane 107 in this storage is an operation as an oxidizer, and when electric field are impressed to the ferroelectric film 102, it is for supplying the oxygen which runs short within the crystal of these ferroelectric film 107. Therefore, 107 may make the glass which contained these oxidizers and an oxidizer in the ferroelectric film 102 that to be P<sub>2</sub>O<sub>5</sub> this phosphorus glass membrane 5 simple substance, and what is necessary is just the film

containing oxidizers, such as the simple substance film, 5 manganese oxide and potassium permanganate of 5 manganese oxide and potassium permanganates other than  $P_2O_5$ , or nitric-acid potash, and nitric-acid potash, contain, or may be mixed. Moreover, the film containing this oxidizer may not necessarily be formed as not only the up front face of the ferroelectric film 102 but a lower front face, or an interlayer. In addition, since oxidizers, such as  $P_2O_5$ , are hygroscopicity, when forming the simple substance film and the high concentration film, they need to form insulator layers, such as low concentration film,  $SiO_2$  film, and  $Si_3N_4$  film, further, and need to improve moisture resistance.

[0011] By enabling it to supply the oxygen from an oxidizer to the ferroelectric film, it can come the number of rewritings of storage, the count of a substitute can be made into 1 billion times or more, and a life can be carried out in 10 or more.

[0012] Drawing 2 is the sectional view of the storage important section of a semiconductor memory showing other examples of this invention. Namely, the diffusion layer 105 of an impurity and  $SiO_2$  film 106 are formed in  $Si_{104}$ , and it changes. A contact hole can open in this  $SiO_2$  film 106, and connect with said diffusion layer 105 and the electrode layer 101 which consists of the Pt/Ti film which is the 1st electrode, the Pt/TiN/TiN film, etc. through this contact hole is formed. Strong \*\*\*\*\* 102 is formed on the electrode layer 101 which is said 1st electrode, and it changes. On this ferroelectric film 102, the electrode layer 103 which consists of the Ti/Pt film which is the 2nd electrode is formed, and it changes. The storage section of a semiconductor memory is formed and it changes, and the with a phosphorus concentration thickness [ about 10–100nm in % and thickness of 4–10 mols ] phosphorus glass membrane 107 is formed in the front face of this storage section which includes the side face of the ferroelectric film 102 at least, and it grows into it.

[0013] An operation of the phosphorus glass membrane 107 in this storage is an operation as an oxidizer, and when electric field are impressed to the ferroelectric film 102, it is for supplying the oxygen which runs short within the crystal of these ferroelectric film 102 from the side face of the ferroelectric film 102. Moreover, 107 may be  $P_2O_5$  this phosphorus glass membrane 5 simple substance, and should just be the film containing oxidizers, such as the simple substance film, manganese oxide and potassium permanganate of 5 manganese oxide and potassium permanganates other than  $P_2O_5$ , or nitric-acid potash, and nitric-acid potash. Moreover, the film containing this oxidizer may not necessarily be formed as not only the up front face of the ferroelectric film 102 but a lower front face, or an interlayer. In addition, since oxidizers, such as  $P_2O_5$ , are hygroscopicity, when forming the simple substance film and the high concentration film, they need to form insulator layers, such as low concentration film,  $SiO_2$  film, and  $Si_3N_4$  film, further, and need to improve moisture resistance.

[0014] Furthermore, this phosphorus glass membrane 107 etches the ferroelectric film 102 the shape for example, of a stripe, and in the shape of a check, or forms irregularity \*\*\*\* about 10–100nm, and forms it in that front face that includes a side face at least, and the electrode layer may be further formed in those upper and lower sides.

[0015] By forming the glass membrane containing an oxidizer or an oxidizer of the

ferroelectric film etc. in a side face at least, it can come the number of rewritings of storage, the count of a substitute can be made into 1 billion times or more, and a life can be carried out in 10 or more.

[0016] Drawing 3 is the sectional view of the storage important section of a semiconductor memory showing the example of others of this invention. Namely, the diffusion layer 105 of an impurity and SiO<sub>2</sub> film 106 are formed in Si104, and it changes. A contact hole can open in this SiO<sub>2</sub> film 106, and the front face of the electrode layer 101 which is this 1st electrode while connecting with said diffusion layer 105, forming the electrode layer 101 which consists of the Pt/Ti film which is the 1st electrode through this contact hole and changing is formed in \*\*, and changes. On the \*\*\*\* electrode layer 101 which is this 1st electrode, the ferroelectric film 102 is formed at least in about 10-100nm by about 10-100nm at \*\*, and the front face turns to it. On the ferroelectric film 102 on this front face of rough, the electrode layer 103 which consists of the Ti/Pt film which is the 2nd electrode is formed, and it changes, and the storage section of a semiconductor memory is formed and it changes.

[0017] Not only a front face but the inside of the ferroelectric film and the bottom front face of the ferroelectric film may make the ferroelectric film rough structure. for example, raise Pori Si for the front face of an electrode 101 at 550 degrees with a CVD method on photoetching etc. and a substrate at a spherical crystal grain, form an electrode 101 on it, after making the front face of an electrode 101 into about 10-100nm concave convex rough structure, form the ferroelectric film 102, or After carrying out spherical crystal granulation of the ferroelectric for the front face of the ferroelectric film 102 with photoetching or a CVD method and making the front face of the ferroelectric film 102 into about 10-100nm concave convex rough structure, you may carry out forming an electrode 103 etc.

[0018] When the ferroelectric film was made into about 10-100nm rough structure and electric field are impressed to the ferroelectric film, according to the difference of the thickness of the ferroelectric film The part which causes polarization, and the part which is not raised arise and there is an operation which can give the so-called self-compensation function to compensate the oxygen atom which deviates from the part which caused polarization with the oxygen atom in the part which has not caused polarization. It can come the number of rewritings of storage, the count of a substitute can be made into 1 billion times or more, and a life can be carried out in 10 or more.

[0019] In addition, it cannot be overemphasized that the ferroelectric film is made into about 10-100nm rough structure, and the glass which contained the oxidizer and the oxidizer in the ferroelectric film may be made to contain, or you may make it, and mix. [ forming the oxidizer film in the front face and side face of the ferroelectric film ]

[0020] In addition, as ferroelectric film, there are others and titanic-acid BARYUUMU and titanic-acid stolon CHUMU, a titanic-acid bismuth, etc. [ lead / titanic-acid zirconium ]

[0021] The approach which, and is contained mixed, or has \*\*\*\*ed the ferroelectric film enough about 10-100nm rough structure, and is carried out [ an approach ] [ forming the glass membrane and the oxidizer film containing an

oxidizer in the front face and side face of this ferroelectric film ] E. The high dielectric film which consists of Fujili, et.al., IEDM Technical Digest, and with a dielectric constant of about 400 shown in 267 (1992) titanic-acid BARYUUMU stolon CHUUMU, P. like C.Fazan et.al., IEDM Technical Digest, the with a dielectric constant of about 21 shown in 263 (1992) tantalum oxide film, etc. Are applicable also to the high dielectric film used for the capacitor storage section of dynamic random access memory. In this case, the leakage current of a high dielectric film can be decreased and increase of memory holding time, extension of the REFURESSHU time amount accompanying it, low-power-ization, etc. can be attained.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] It is the theoretic sectional view of the storage section showing one example of this invention.

[Drawing 2] It is the sectional view of the storage important section of a semiconductor memory showing other examples of this invention.

[Drawing 3] It is the sectional view of the storage important section of a semiconductor memory showing the example of others of this invention.

### [Description of Notations]

- 101 ... Electrode layer
- 102 ... Ferroelectric film
- 103 ... Electrode layer
- 104 ... Si
- 105 ... Diffusion layer
- 106 ... SiO<sub>2</sub> film
- 107 ... Phosphorus glass membrane

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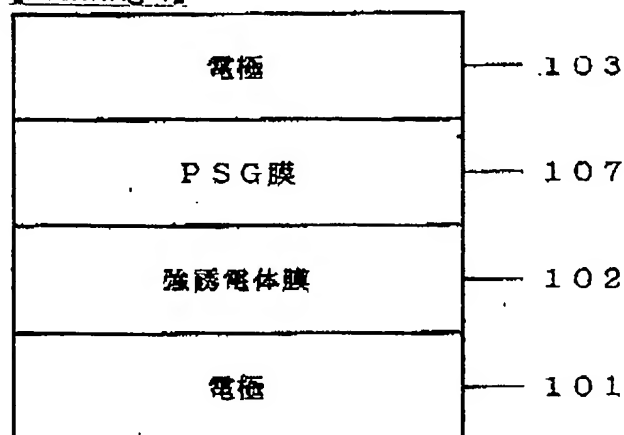
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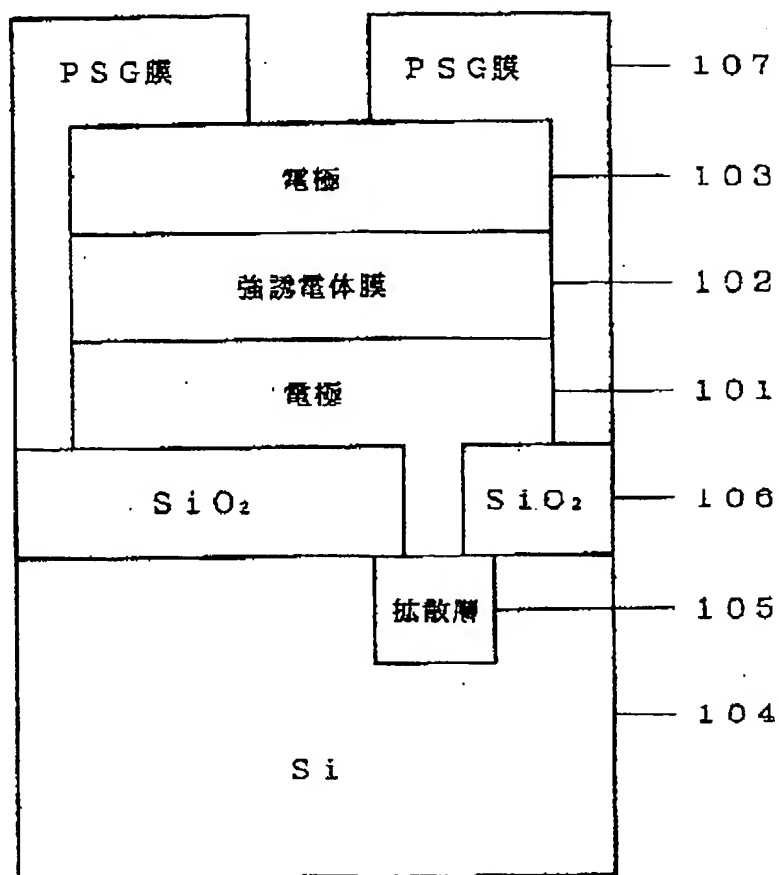
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DRAWINGS

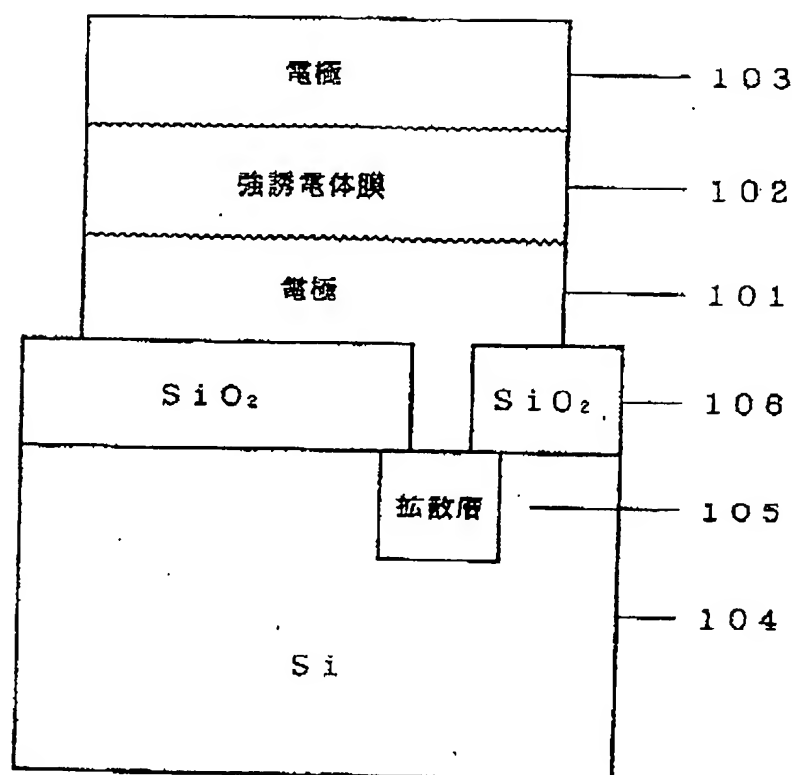
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[Drawing 1][Drawing 2]



[Drawing 3]





[Translation done.]

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